

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Zinc is an element commonly found in the earth's crust. It is released to the environment both from natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgic operations involving zinc and use of commercial products containing zinc. Worldwide, releases to soil are probably the greatest source of zinc in the environment. The most important sources of zinc in soil are discharges of smelter slags and wastes, mine tailings, coal and bottom fly ash, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. Zinc does not volatilize from soil. Although zinc usually remains adsorbed to soil, leaching has been reported at waste disposal sites. Zinc does not volatilize from water but is deposited primarily in sediments through adsorption and precipitation. Severe zinc contamination tends to be confined to areas near emission sources.

Zinc is capable of forming complexes with a variety of organic and inorganic groups (ligands). Biological activity can affect the mobility of zinc in the aquatic environment, although the biota contains relatively little zinc compared to the sediments. Zinc bioconcentrates moderately in aquatic organisms; bioconcentration is higher in crustaceans and bivalve species than in fish. Zinc does not concentrate in plants, and it does not biomagnify through terrestrial food chains.

There are few data regarding the speciation of zinc released to the atmosphere. Zinc is removed from the air by dry and wet deposition, but zinc particles with small diameters and low densities suspended in the atmosphere travel long distances from emission sources.

Zinc has been detected in air, surface water, groundwater, and soil; the frequency of detection and the concentrations are greatest near source areas (e.g., hazardous waste sites and industrial areas such as lead smelters). In a survey by the National Air Surveillance Network, the mean concentration of zinc in the air in the United States in 1977-1979 was 0.02-0.16 $\mu\text{g}/\text{m}^3$ for urban air compared to 0.01-0.05 $\mu\text{g}/\text{m}^3$ for rural air. The concentrations of zinc in the air of remote areas range from <0.003 to 0.027 $\mu\text{g}/\text{m}^3$. The mean concentrations of zinc in ambient water and drinking water range from 0.02 to 0.05 mg/L and from 0.01 to 0.1 mg/L, respectively. The

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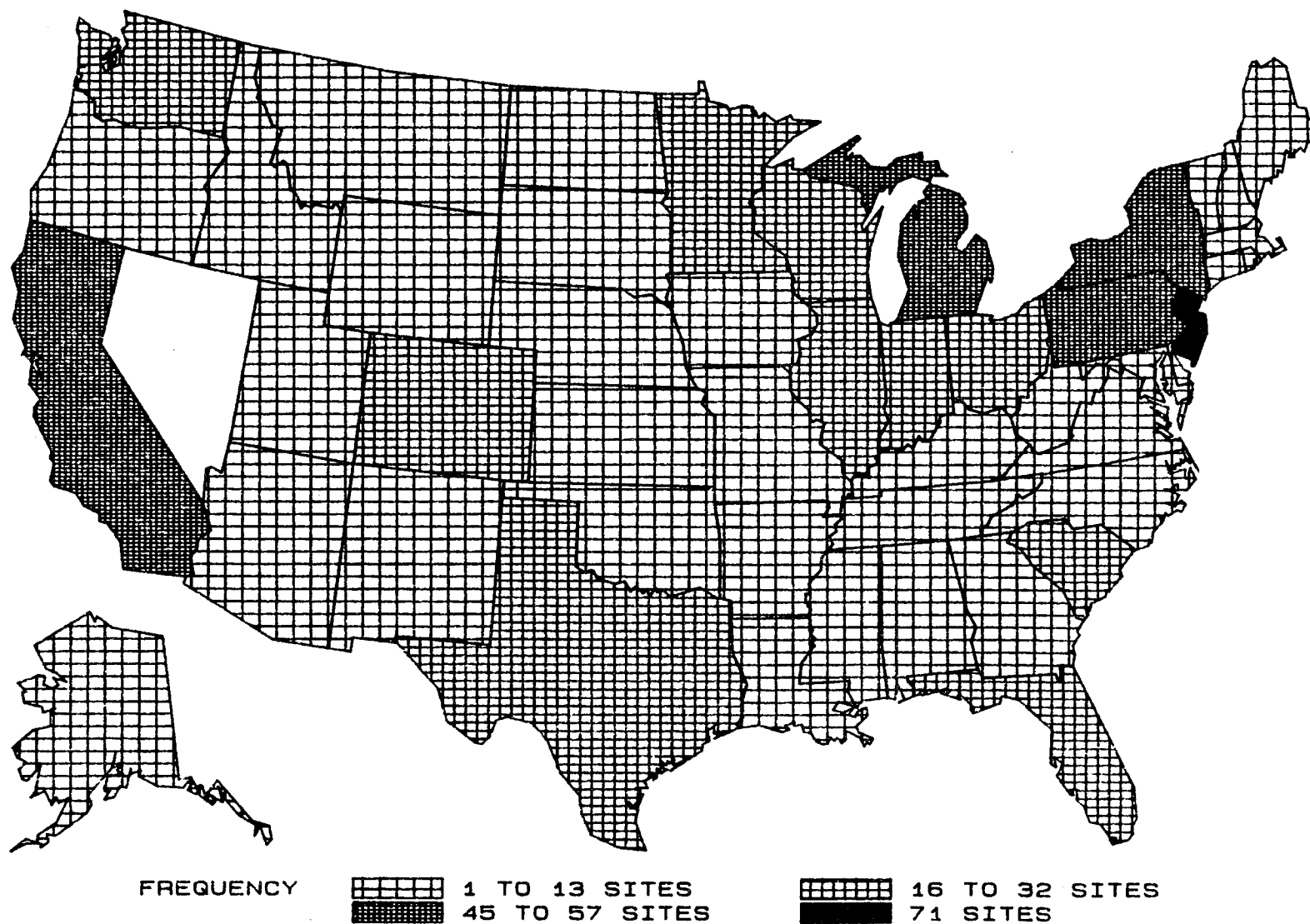
concentration of zinc in drinking water can often be higher than the concentration in the raw water from which the drinking water was obtained because zinc may leach from transmission and distribution pipes. The concentration of zinc in standing water from galvanized household water pipes was ≤ 1.3 mg/L (Sharrett et al. 1982a). The concentration of zinc in cultivated soils in the United States ranged from <5 to 400 mg/kg, with a mean of 36 mg/kg, compared to a range of <10 -2,000 mg/kg, with a mean of 51 mg/kg, in uncultivated soils; this probably results from the differences in soils used for farming rather than the use of zinc in agriculture. Concentrations of zinc can be high in soils from contaminated sites, such as waste dumps. Zinc has been identified in at least 776 of the 1,350 NPL hazardous waste sites (HAZDAT 1993). However, the number of sites evaluated for zinc is not known. The frequency of these sites can be seen in Figure 5-1. Seven sites are located in the Commonwealth of Puerto Rico (not shown).

The concentrations of zinc in various foods and human tissues have also been determined. In a 1980-1982 survey of total diet samples, the Food and Drug Administration (FDA) estimated that the average intake of zinc from food (including water) for an adult was 0.23 mg/kg/day. The FDA concluded that the daily intake of zinc from the inhalation of ambient air is negligible compared to the daily intake from food. Certain population groups may be exposed to higher concentrations of zinc than the general population. People who work in coal mines, people who work with the refining and smelting of nonferrous metals, and people who live near waste sites and metal smelting operations may be exposed to high levels of zinc. People who consume large amounts of foods high in zinc content, such as oysters and mussels, may also be exposed to high levels of zinc. The higher exposure may not always be manifested as increased body burden in the exposed individuals.

5.2 RELEASES TO THE ENVIRONMENT

Zinc is commonly found in the earth's crust, and natural releases to the environment can be significant. In addition, zinc is one of the most widely used metals in the world. The major industrial sources of zinc include electroplating, smelting and ore processing, and drainage from both active and inactive mining operations (Mirenda 1986). Furthermore, zinc is an important component of brass, bronze, die casting metal, other alloys, rubber, and paints. The environmental releases of zinc from anthropogenic sources far exceed the releases from natural sources (Fishbein 1981).

FIGURE 5-1. FREQUENCY OF NPL SITES WITH ZINC CONTAMINATION *



*Derived from HazDat 1993

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5.2.1 Air

Zinc is released to the atmosphere as dust and fumes from zinc production facilities, lead smelters, brass works, automobile emissions, fuel combustion, incineration, and soil erosion. Refuse incineration, coal combustion, smelter operations, and some metal-working industries constitute the major sources of zinc in air (EPA 1980d; Ragaini et al. 1977). Estimated atmospheric zinc loss is 100 g/ton of zinc mined, and most of the loss comes from handling raw and concentrated ore and wind erosion of tailing piles (Lloyd and Showak 1984). Average zinc emissions to the atmosphere from stationary sources in the United States were 151,000 tons/year for 1969-1971 (Fishbein 1981). An estimated projection of zinc emission for 1983, based on production estimates and assuming no changes in processes or control technology, was 273,000 tons/year. The estimated worldwide emission of zinc to the atmosphere in 1983 was 70,250-193,500 metric tons. Emissions from zinc-cadmium production, steel and iron manufacture, and copper-nickel production were estimated to be the principal atmospheric sources of zinc (Nriagu and Pacyna 1988). According to the TRI, an estimated total of 1,933,687 pounds of zinc, amounting to about 17% of the total environmental release, was discharged into the atmosphere in the United States in 1991 from the manufacturing and processing facilities listed in Table 5-1 (TR191 1993). The TRI data should be used with caution since only certain facilities are required to report. Table 5-1 is not an exhaustive list.

5.2.2 Water

Zinc and its compounds are found in the earth's crust and are present in most rocks, certain minerals, and some carbonate sediments. As a result of the weathering of these materials, soluble compounds of zinc are formed and may be released to water (NAS 1977). The largest input of zinc to water results from erosion of soil particles containing natural traces of zinc (45,400 metric tons/year) (EPA 1980d). Erosion resulting from human activities accounts for 70% of this soil loss; geologic or natural erosion constitutes the other 30% (EPA 1980d). However, this source of low levels of zinc is widely dispersed and is, therefore, unlikely to elevate aquatic concentrations significantly.

TABLE 5-1. Releases to the Environment from Facilities
That Manufacture or Process Zinc (Fume or Dust)^a

State ^c	Number of facilities	Range of reported amounts released in thousands of pounds ^b						
		Air	Underground injection	Water	Land	Total Environment ^d	POTW ^e transfer	Off-site waste transfer
AL	21	0.0-39.1	0.0-0.0	0.0-0.3	0.0-49.5	0.0-83.2	0.0-0.8	0.0-13.0
AR	11	0.0-1.4	0.0-0.0	0.0-0.3	0.0-114.5	0.0-115.5	0.0-0.3	0.0-4.5
AZ	3	0.3-15.8	0.0-0.0	0.0-0.0	0.0-20.6	0.3-36.3	0.0-0.0	0.0-14.7
CA	36	0.0-7.6	0.0-0.0	0.0-0.0	0.0-0.0	0.0-7.6	0.0-0.3	0.0-24.0
CO	2	0.0-0.3	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.3	0.0-0.0	0.3-60.0
CT	6	0.0-8.4	0.0-0.0	0.0-0.3	0.0-28.5	0.0-37.2	0.0-0.0	0.0-124.4
FL	8	0.0-1.2	0.0-0.0	0.0-0.0	0.0-0.3	0.0-1.2	0.0-0.0	0.0-0.8
GA	9	0.0-12.0	0.0-0.3	0.0-0.8	0.0-67.0	0.0-79.0	0.0-0.0	0.0-27.0
IA	12	0.0-35.1	0.0-0.0	0.0-1.7	0.0-0.0	0.0-36.8	0.0-0.0	0.0-12.3
IL	48	0.0-145.0	0.0-0.0	0.0-2.2	0.0-2627.0	0.0-2773.8	0.0-1.7	0.0-321.8
IN	32	0.0-14.8	0.0-0.0	0.0-0.3	0.0-39.8	0.0-39.8	0.0-1.8	0.0-64.9
KY	13	0.0-20.7	0.0-0.0	0.0-3.9	0.0-2.8	0.0-25.8	0.0-0.3	0.0-357.7
LA	7	0.0-31.7	0.0-0.0	0.0-0.0	0.0-0.1	0.0-31.7	0.0-0.0	0.0-118.7
MA	8	0.0-1.0	0.0-0.0	0.0-0.3	0.0-0.0	0.0-1.3	0.0-0.3	0.0-3.5
MD	8	0.0-1.0	0.0-0.0	0.0-0.0	0.0-0.0	0.0-1.0	0.0-0.3	0.0-12.3
ME	3	0.0-2.8	0.0-0.0	0.0-0.0	0.0-0.0	0.0-2.8	0.0-0.0	5.9-15.5
MI	27	0.0-140.0	0.0-0.0	0.0-0.0	0.0-5880.0	0.0-5980.6	0.0-0.8	0.0-54.0
MN	11	0.0-22.7	0.0-0.0	0.0-0.0	0.0-0.0	0.0-22.7	0.0-2.5	0.0-11.3
MO	18	0.0-5.1	0.0-0.0	0.0-0.0	0.0-0.3	0.0-5.1	0.0-0.3	0.0-44.4
MS	3	0.0-0.0	0.0-0.0	0.0-0.0	0.0-10.0	0.0-10.0	0.0-0.1	0.0-0.8
NC	15	0.0-5.5	0.0-0.0	0.0-0.3	0.0-0.3	0.0-5.5	0.0-1.8	0.0-60.5
NE	3	0.1-6.9	0.0-0.0	0.0-0.0	0.0-0.0	0.1-6.9	0.0-0.0	0.0-0.3
NH	1	0.5-0.5	0.0-0.0	0.0-0.0	0.0-0.0	0.5-0.5	0.0-0.0	0.0-0.0
NJ	14	0.0-6.2	0.0-0.0	0.0-0.0	0.0-0.3	0.0-6.2	0.0-1.0	0.0-2833.2
NM	1	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0	11.0-11.0	0.0-0.0
NV	1	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.0
NY	12	0.0-26.9	0.0-0.0	0.0-0.0	0.0-0.0	0.0-26.9	0.0-1.1	0.0-92.6
OH	46	0.0-27.1	0.0-0.0	0.0-0.3	0.0-3.3	0.0-27.3	0.0-1.3	0.0-2195.8
OK	9	0.0-4.6	0.0-0.0	0.0-0.0	0.0-0.3	0.0-4.6	0.0-0.4	0.0-1246.9
OR	5	0.0-45.7	0.0-0.0	0.0-0.1	0.0-0.3	0.0-45.7	0.0-0.0	0.0-0.8
PA	31	0.0-45.1	0.0-0.0	0.0-1.0	0.0-4.7	0.0-45.9	0.0-0.3	0.0-115.0
PR	6	0.0-0.3	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.3	0.0-2.0	0.0-8.5
RI	5	0.0-0.5	0.0-0.0	0.0-0.0	0.0-0.0	0.0-0.5	0.0-0.3	0.0-2.5
SC	13	0.0-68.7	0.0-0.0	0.0-0.0	0.0-0.3	0.0-68.7	0.0-0.3	0.0-92.0
SD	1	0.3-0.3	0.0-0.0	0.0-0.0	0.0-0.0	0.3-0.3	0.0-0.0	0.0-0.0
TN	13	0.0-133.0	0.0-0.0	0.0-2.8	0.0-2244.2	0.0-2379.9	0.0-0.3	0.0-16.1
TX	22	0.0-48.0	0.0-0.0	0.0-11.1	0.0-4.0	0.0-48.0	0.0-0.0	0.0-39.6
UT	1	36.7-36.7	0.0-0.0	0.0-0.0	0.0-0.0	36.7-36.7	0.0-0.0	119.7-119.7

TABLE 5-1 (continued)

State ^c	Number of facilities	Range of reported amounts released in thousands of pounds ^b						
		Air	Underground injection	Water	Land	Total Environment ^d	POTW ^e transfer	Off-site waste transfer
VA	13	0.0-102.0	0.0-0.0	0.0-4.3	0.0-18.0	0.0-102.0	0.0-0.3	0.0-169.7
VT	1	0.3-0.3	0.0-0.0	0.0-0.0	0.0-0.0	0.3-0.3	0.0-0.0	0.3-0.3
WA	5	0.0-24.2	0.0-0.0	0.0-0.0	0.0-0.0	0.0-24.2	0.0-0.0	0.0-1.9
WI	25	0.0-85.6	0.0-0.0	0.0-1.3	0.0-27.7	0.0-114.6	0.0-0.3	0.0-75.2
WV	6	0.0-19.3	0.0-0.0	0.0-0.0	0.0-0.0	0.0-19.3	0.0-0.0	0.0-6.8

^aDerived from TRI90 (1992)

^bData in TRI are maximum amounts released by each facility. Quantities reported here have been rounded to the nearest hundred pounds, except those quantities > 1 million pounds which have been rounded to the nearest thousand pounds.

^cPost Office state abbreviation

^dThe sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility.

^ePOTW = publicly owned treatment works

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Urban runoff, mine drainage, and municipal and industrial effluents are smaller but more concentrated sources of zinc in water. Industries that discharge large quantities of zinc directly to water include iron and steel, zinc smelting, plastics, and electroplating (EPA 1980d). The arithmetic mean concentration of zinc in influents of 239 waste-water treatment plants in the United States was 0.7 mg/L, with minimum and maximum concentrations of 0.0001 and 28.7 mg/L, respectively (Minear et al. 1981). Accidental zinc discharges to water are most often associated with smelting and refining operations. Zinc is present with cadmium and lead in these processes (NAS 1977). Urban runoff and drainage from inactive mines account for approximately 5,250 and 4,060 metric tons/year, respectively, of the total releases of zinc to water (EPA 1980d). Drainage from active mining areas is considerably less than from inactive areas because of the disposal methods currently employed. Hazardous waste sites, in which zinc has been improperly disposed of, are additional sources of the element.

Metals, such as zinc, also enter estuaries from many natural and man-made sources. Three important sources of zinc input into surface water are metal manufacturing, domestic waste water, and atmospheric fallout. On an annual worldwide basis, an estimated 77,000-375,000 metric tons of zinc are discharged into water from anthropogenic sources (Nriagu and Pacyna 1988). Publicly owned treatment works are the largest total point source for zinc discharges. Publicly owned treatment works receive zinc contributions from the water supply and distribution system corrosion, combined sewer area runoff, industrial wastes, and human excrement (EPA 1980d). According to the TRI, publicly owned treatment works discharged 30,466 pounds of zinc into the environment, whereas manufacturing and processing facilities listed in Table 5-1 discharged an estimated 28,080 pounds of zinc (amounting to much less than 1% of the total environmental release) into surface waters in the United States in 1991 (TR191 1993). The TRI data should be used with caution since only certain types of facilities are required to report output. Table 5-1 is not an exhaustive list.

The concentration of zinc in drinking water may increase as a result of the distribution system and household plumbing (EPA 1987~). Common piping materials used in distribution systems often contain zinc, as well as other metals and alloys. Trace metals may enter the water through corrosion products or simply by the dissolution of small amounts of metals with which the water comes in contact. Reactions with materials of the distribution system, particularly in soft low-pH waters, very often have produced concentrations of zinc in tap water much greater than those in

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the raw or treated waters at the plant of origin (NAS 1977). The total quantity of annual releases of zinc from these sources has not been estimated.

5.2.3 Soil

Limited information is available on total releases of zinc to soil. Zinc is often present in soils and grasses as a result of atmospheric deposition. Furthermore, approximately 22,000 tons of zinc are used in fertilizers each year in the United States (NAS 1977). The extent to which zinc may run off into soil, rivers, and streams has not been evaluated. Hazardous waste sites are additional sources of zinc in soil. Municipal sludges applied to cropland soils can also be an important source of trace metals, including zinc (Chang et al. 1987).

On a worldwide basis, an estimated 1,193,000-3,294,000 metric tons of zinc per year are released to soil from anthropogenic sources (Nriagu and Pacyna 1988). The four most important sources of zinc in soil were estimated to be smelter slugs and wastes, mine tailings, coal and bottom fly ash, and the discharge of commercial products such as fertilizers. According to the TRI, an estimated total of 9,216,574 pounds of zinc, amounting to about 82% of the total environmental release in the United States, was released to soil in the United States in 1991 from the manufacturing and processing facilities listed in Table 5-1 (TR191 1993). An estimated total of 115 pounds was released through underground injection, and another 73,000,000 pounds were transferred to off-site treatment, storage, and disposal facilities. The TRI data should be used with caution since only certain types of facilities are required to report. Table 5-1 is not an exhaustive list.

5.3 ENVIRONMENTAL FATE

Zinc occurs in the environment mainly in the +2 oxidation state (Lindsay 1979). Sorption is the dominant reaction, resulting in the enrichment of zinc in suspended and bed sediments (Callahan et al. 1979). Zinc in aerobic waters is partitioned into sediments through sorption onto hydrous iron and manganese oxides, clay minerals, and organic material. The efficiency of these materials in removing zinc from solution varies according to their concentrations, pH, redox potential (Eh), salinity, nature and concentrations of complexing ligands, cation exchange capacity, and the concentration of zinc. Precipitation of soluble zinc compounds appears to be significant only

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under reducing conditions in highly polluted water. Generally, at lower pH values, zinc remains as the free ion. The free ion (Zn^{+2}) tends to be adsorbed and transported by suspended solids in unpolluted waters. In polluted waters in which the concentration of zinc is high, removal of zinc by precipitation of the hydroxide is possible, particularly when the pH is greater than 8.0 (Callahan et al. 1979). In anaerobic environments and in the presence of sulfide ions, precipitation of zinc sulfide limits the mobility of zinc. The relative mobility of zinc in soil is determined by the same factors that affect its transport in aquatic systems (i.e., solubility of the compound, pH, and salinity) (Clement 1985).

Zinc is an essential nutrient that is present in all organisms. Although biota appears to be a minor reservoir of zinc relative to soils and sediments, microbial decomposition of biota in water can produce ligands, such as humic acids, that can affect the mobility of zinc in the aquatic environment through zinc precipitation and adsorption (Callahan et al. 1979).

Zinc concentrations in the air are relatively low, except near industrial sources such as smelters. No estimate for the atmospheric lifetime of zinc is available at this time, but the fact that zinc is transported long distances in air indicates that its lifetime in air is at least on the order of days.

5.3.1 Transport and Partitioning

The tendency of a chemical to partition between soil, water, sediment, air, and biota can be inferred from its physical and/or chemical properties. Zinc occurs in the environment primarily in the +2 oxidation state. It dissolves in acids to form hydrated Zn^{+2} cations and in strong bases to form zincate anions (probably $\text{Zn}[\text{OH}]_4^{-2}$). In most unpolluted waters, zinc exists primarily as the hydrated form of the divalent cation. In polluted waters, the metal often forms complexes with a variety of organic and inorganic ligands (Callahan et al. 1979; EPA 1984b, 1987c).

Zinc can occur in both suspended and dissolved forms in surface water. Dissolved zinc may occur as the free (hydrated) zinc ion or as dissolved complexes and compounds with varying degrees of stability. Suspended (undissolved) zinc may be dissolved following minor changes in water chemistry or may be sorbed to suspended matter.

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In the aquatic environment, zinc partitions to sediments or suspended solids in surface waters through sorption onto hydrous iron and manganese oxides, clay minerals, and organic material. Reservoirs located downstream from lead-zinc mining and milling areas were found to contain higher concentrations of zinc than reservoirs in other areas, and the zinc was more highly concentrated in reservoir bottom sediments than in the surrounding soils (Pita and Hyne 1975). In addition, the zinc content in sediment closely correlated with the depth, organic content, and clay content of the sediments. Phosphates and iron hydroxides play an important role in the transfer of heavy metals (and presumably zinc) from river water to the sediments, according to a study by Houba et al. (1983). In this study, zinc was bound predominantly to carbonate and amorphous matter (iron, aluminum, and manganese hydroxides). In addition, mobile components of naturally occurring organic matter contributed to the increase in the metal hydroxide-bound fraction.

The transport of zinc in the aquatic environment is controlled by anion species. In natural waters, complexing agents, such as humic acid, can bind zinc. The stability of the zinc complex depends on the pH of the water and the nature of the complex. The dissociation of the complex may determine the amount of zinc in solution. Zinc in humic acid complex may be 50% dissociated at pH 5.5, and the dissociation rate may be higher as the pH decreases (Guy and Chakrabarti 1976). Therefore, as the pH of the water decreases, the concentration of zinc ions in the water phase increases at the same rate as that of the release of zinc from the sediment. The magnesium found in the silicate minerals of igneous rocks is often replaced with the divalent zinc ion; consequently, weathering of this zinc-containing bedrock gives rise to Zn^{+2} in solution. The hydrated cation is the dominant form when the pH is ≤ 9 (Callahan et al. 1979).

The tendency of zinc to be sorbed is affected not only by the nature and concentration of the sorbent but also by pH and salinity (Callahan et al. 1979). Zinc tends to sorb more readily at a high pH (pH >7) than at a low pH (Callahan et al. 1979). Desorption of zinc from sediments occurs as salinity increases (Helz et al. 1975), apparently because of displacement of the adsorbed zinc ions by alkali and alkaline earth cations, which are abundant in brackish and saline waters (Callahan et al. 1979). In column leaching tests with sediment collected from the banks of the Rhone River, the presence of dissolved organic matter and pH was found to be the factors controlling the adsorption and mobility of zinc (Bourg and Darmendrail 1992).

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A small fraction of the zinc initially exists in the aquatic phase as soluble inorganic zinc compounds. Zinc chloride and zinc sulfate are very soluble in water but hydrolyze in solution to form a zinc hydroxide precipitate. Hydrolysis may lower pH, but the buffering action present in most natural water prevents a significant alteration in pH. The precipitation of zinc hydroxide and zinc carbonate was studied by Patterson et al. (1977) who found that zinc hydroxide precipitates faster than zinc carbonate. Zinc carbonate is soluble in pure water at 25°C at concentrations of ≤ 107 mg zinc/L. The hydroxide is soluble only at concentrations of ≤ 0.2 mg zinc/L. As a result, some of the inorganic forms of zinc that are expected to be present in water are basic carbonate ($\text{Zn}_2[\text{OH}]_2\text{CO}_3$), hydroxide ($\text{Zn}[\text{OH}]_2$) and silicate (Zn_2SiO_4) (Florence 1980; NAS 1977). When the pH is ≥ 8 , most of these compounds will precipitate; however, as the pH decreases, more and more of these compounds will dissolve and remain in the water phase (Callahan et al. 1979).

The effect of pH on the mobilization of zinc in a few highly acidic clean lakes has been studied (Sprenger et al. 1987; White and Driscoll 1987). In these lakes, in which the pH was ≤ 3.6 , concentrations of zinc were elevated in the water column, and the concentration of zinc in the upper layer of sediment was substantially lower than values reported for other lakes at higher pH values. The relatively higher concentration of zinc in the water column compared to the sediment may be the result of lower adsorption of zinc on oxide surfaces due to low pH, solubilization of inorganic zinc from the sediment layer, and the dissociation of bound organic complexes of zinc present in the sediment and their subsequent release into the water phase.

The precipitation of zinc sulfide is an important control on the mobility of zinc in reducing environments where hydrogen sulfide is formed. The precipitation of the hydroxide, carbonate, or basic sulfate may become more significant at high concentrations in highly polluted water. The hydroxides and hydrous oxides of iron and manganese are often components of the clay fraction of sediments and often exist as coatings on the surfaces of other minerals (NAS 1977). Zinc may coprecipitate with hydrous oxides when reduced iron or manganese oxides are oxidized. As the new solids are formed, they can trap various ions in their crystal lattice (Callahan et al. 1979).

Zinc sorbs strongly onto soil particulates. Little water-soluble and exchangeable heavy metals were found in soil irrigated with raw waste water (Schalscha et al. 1982). Although considerable amounts of metals were added to the soil in soluble and exchangeable forms during waste-water

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irrigation, they were converted into the less chemically active forms (i.e., organically bonded and inorganic precipitates). Further examination showed that zinc accumulation in soil resulting from waste disposal occurred primarily in inorganic precipitates.

The mobility of zinc in soil depends on the solubility of the speciated forms of the element and on soil properties such as cation exchange capacity, pH, redox potential, and chemical species present in soil; under anaerobic conditions, zinc sulfide is the controlling species (EPA 1980d; Kalbasi et al. 1978). Since zinc sulfide is insoluble, the mobility of zinc in anaerobic soil is low. In a study of the effect of pH on zinc solubility, Saeed and Fox (1977) showed that, when the pH is <7 , an inverse relationship exists between the pH and the amount of zinc in solution. As negative charges on soil surfaces increase with increasing pH, additional sites for zinc adsorption are activated and the amount of zinc in solution decreases. The active zinc species in the adsorbed state is the singly charged zinc hydroxide species (i.e., $\text{Zn}[\text{OH}]^+$) (Sanders and Kherbawy 1987). Other investigators have also shown that the mobility of zinc in soil increases at lower soil pH under oxidizing conditions and at a lower cation exchange capacity of soil (Bergkvist et al. 1989; Hermann and Neumann-Mahlkau 1985; Tyler and McBride 1982). On the other hand, the amount of zinc in solution generally increases when the pH is >7 in soils high in organic matter. This is probably a result of either the release of organically complexed zinc, reduced zinc adsorption at higher pH, or an increase in the concentration of chelating agents in soil (Saeed and Fox 1977). For calcareous soils, the relationship between zinc solubility and pH is nonlinear. At a high pH, zinc in solution is precipitated as $\text{Zn}(\text{OH})_2$, zinc carbonate (ZnCO_3), or calcium zincate (Saeed and Fox 1977). Clay and metal oxides are capable of sorbing zinc and tend to retard its mobility in soil. Soil distribution constants (K_d) of 100 ± 770 mL/g for sandy loam soil and 0.2 ± 4 mL/g for sandy soils were reported by Gerritse et al. (1982). A K_d of $0.1 \pm 8,000$ mL/g was reported by Baes and Sharp (1983), but an average K_d of 40 mL/g was reported by Baes et al. (1984).

Zinc in a soluble form, such as zinc sulfate, is fairly mobile in most soils. However, relatively little land-disposed zinc is in the soluble form, and mobility is, therefore, limited by a slow rate of dissolution. Consequently, movement towards groundwater is expected to be slow unless zinc is applied to soil in soluble form (such as in agricultural applications) or accompanied by corrosive substances (such as in mine tailings) (EPA 1980d). Yet, soil conditions not suitable for zinc

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sorption may lead to leaching. Low pH ($\text{pH} < 7$) and high ionic strength of the leaching solution favor desorption (EPA 1987c; Saeed and Fox 1977).

Zinc is an essential nutrient and occurs in the tissues of organisms, even at normal ambient water and soil concentrations. Zinc can accumulate in freshwater animals at 51-1,130 times the concentration present in the water (EPA 1987c). Microcosm studies indicate, in general, that zinc does not biomagnify through food chains (Biddinger and Gloss 1984; Callahan et al. 1979; Hegstrom and West 1989). Furthermore, although zinc actively bioaccumulates in aquatic systems, biota appears to represent a relatively minor sink compared to sediments. Steady-state zinc bioconcentration factors (BCFs) for 12 aquatic species range from ≈ 4 to 24,000 (EPA 1987c). Crustaceans and fish can accumulate zinc from both water and food. A BCF of 1,000 was reported for both aquatic plants and fish, and a value of 10,000 was reported for aquatic invertebrates (Fishbein 1981). The order of enrichment of zinc in different aquatic organisms was as follows (zinc concentrations in $\mu\text{g/g}$ dry weight appear in parentheses): fish (23), shrimp (50), mussel (60), periphyton (260), zooplankton (330), oyster (3,300) (Ramelow et al. 1989). The high enrichment in oysters may be due to their ingestion of particulate matter containing higher concentrations of zinc than does ambient water. Other investigators have also indicated that organisms associated with sediments have higher zinc concentrations than organisms living in the aqueous layer (Biddinger and Gloss 1984). With respect to bioconcentration from soil by terrestrial plants, invertebrates, and mammals, BCFs of 0.4, 8, and 0.6, respectively, have been reported. The concentration of zinc in plants depends on the plant species, soil pH, and the composition of the soil (Dudka and Chlopecka 1990; Rudd et al. 1988). Plant species do not concentrate zinc above the levels present in soil (Levine et al. 1989).

Wind-blown dust transports zinc bound to soil particulates into the atmosphere (EPA 1980d). The particulates may also contain other materials (Pacyna et al. 1989; Saltzman et al. 1985). Zinc-bearing particles in the atmosphere are transported to soil and water by wet deposition (rain and snow) and dry deposition (gravitational settling and deposition on water and soil surfaces). The detection of zinc in rainwaters (at concentrations higher than atmospheric particles) confirms the importance of wet precipitation in the removal of zinc particles from the atmosphere (Aten et al. 1983; Colin et al. 1990; Dasch and Wolff 1989; Heaton et al. 1990). Zinc particles with low dry deposition velocities (i.e., particles with small diameters and low densities) can be transported from their emission source to distant regions (Pacyna et al. 1989).

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5.3.2 Transformation and Degradation

The transformation of zinc compounds can occur as a result of changes in chemical speciation, such as the formation of zinc oxide in the atmosphere, the hydrolysis of hydrated zinc cations, or the oxidation/reduction of organic and inorganic zinc complexes.

5.3.2.1 Air

The chemical interaction of zinc compounds in the atmosphere may change the anionic speciation of the compound. Atmospheric interactions are greatest for particles with small aerodynamic diameters (Fishbein 1981). Zinc is found in the atmosphere at the highest concentrations in the smallest particles (Fishbein 1981). Atmospheric emissions of zinc, consisting primarily of zinc sorbed to submicron particulate matter in the form of zinc oxide, are expected to dissipate quickly as a result of deposition to soil and surface waters (EPA 1980d).

In the atmosphere, zinc-bearing particles may undergo chemical transformation before deposition. The association of zinc particles in aerosols in Arizona was studied, and five zinc-bearing particles were identified with an automated scanning electron microscope (Anderson et al. 1988). These particles, in decreasing order of concentration in the aerosol, were zinc sulfide, ferrous zinc, zinc phosphides, zinc chloride, and metallic zinc. The presence of zinc sulfide in an area adjacent to mining and smelting activities is not surprising, but no conclusion regarding the speciation of zinc in the atmosphere can be drawn from this investigation. However, the relative concentration of zinc ions in rainwater from a rural area was one order of magnitude higher than in airborne particulates (Aten et al. 1983). This finding suggests that zinc sulfide in the atmosphere is oxidized to a more water-soluble form, zinc sulfate.

5.3.2.2 Water

Zinc is in the +2 form in aqueous solution and exhibits amphoteric properties; it dissolves in acids to form hydrated Zn^{+2} cations and in strong bases to form zincate anions (probably $\text{Zn}[\text{OH}]_4^{-2}$) (Callahan et al. 1979). However, at the pH of most natural waters, the formation of anionic zinc species is not likely.

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A small part of the available zinc may partition into the aquatic phase through the formation of soluble zinc chloride and sulfate compounds. These compounds hydrolyze in solution to form the hydroxide or hydrated zinc oxide precipitate with the resultant decrease in pH. The decrease in pH may increase the solubility of zinc hydroxide and increase the zinc concentration in water. However, the buffering action of most natural waters prevents any significant change of pH due to the hydrolysis reactions. As a result, in the water phase, the solubility of its carbonate and hydroxide is likely to control the availability of zinc. It was reported by Patterson et al. (1977) that $\text{Zn}(\text{OH})_2$ precipitates faster than ZnCO_3 . Zinc is not directly affected by changes in Eh; however, the valences and reactivity of ligands reacting with zinc are affected by Eh. Zinc is an active reducing agent for many ions such as iron (Fe^{+3}) and permanganate (MnO_4^{-2}) ions (Stokinger 1981). As a result of the reducing reactions, the manganese oxides and ferric salts may precipitate out and, in the process, may entrap soluble zinc in the precipitate, thereby reducing the zinc concentration in the water phase.

Because alkyl zinc compounds are unstable in water and oxygen, biomethylation of zinc compounds in aquatic ecosystems probably does not occur (Callahan et al. 1979). No evidence was found that photolysis in the aquatic environment significantly affects the fate of zinc compounds.

5.3.2.3 Sediment and Soil

No information specifically related to transformation and degradation in sediment and soil was identified in the available literature. However, chemical speciation of zinc in sediment and soil is probably affected by the same factors affecting its fate in water. The sediment and soil chemistry of zinc are governed primarily by the pH and the physical properties of sediment and soil. In acidic sediments and soils, more zinc is available in ionic forms, and cation exchange processes influence its fate. Depending on the nature and concentrations of other mobile metals in sediments and soils, competition for the binding sites probably occurs. In the absence of suitable binding sites, zinc may be mobilized (ICF 1986). In alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands.

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5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Zinc concentrations in air are relatively low and fairly constant except near sources such as smelters. Average atmospheric concentrations of zinc resulting from releases from automobiles, fuel combustion, incineration, soil erosion, and industrial, commercial, and construction activity throughout the United States generally are less than $1 \mu\text{g}/\text{m}^3$ (EPA 1980d; Lloyd and Showak 1984). Data on zinc concentrations in New York City during 1972-1975 show that the average atmospheric zinc concentration ranged from 0.293 to $0.380 \mu\text{g}/\text{m}^3$ annually (Lioy et al. 1978). An average ambient zinc concentration of $0.127 \mu\text{g}/\text{m}^3$ (concentration range, $0.027\text{--}0.500 \mu\text{g}/\text{m}^3$) was determined from analyses of particulate samples collected at nine air monitoring sites in the San Francisco Bay area (John et al. 1973). The concentrations of zinc in atmospheric samples collected from seven cities in the United States during 1968-1971 ranged from 0.17 to $0.67 \mu\text{g}/\text{m}^3$, whereas the concentrations at two rural sites ranged from 0.02 to $0.16 \mu\text{g}/\text{m}^3$ (Saltzman et al. 1985). The concentrations of zinc during 1977-1979 from the National Air Surveillance Networks were reported by Evans et al. (1984). The arithmetic mean zinc concentrations in urban areas in the United States ranged from 0.02 to $0.16 \mu\text{g}/\text{m}^3$, whereas the concentrations in non-urban areas ranged from 0.01 to $0.05 \mu\text{g}/\text{m}^3$. The geometric mean concentrations of zinc from three urban areas in New Jersey monitored more recently (1981-1982) ranged from 0.07 to $0.59 \mu\text{g}/\text{m}^3$, whereas the concentrations at a rural site ranged from 0.02 to $0.06 \mu\text{g}/\text{m}^3$ (Daisey 1987). The reported concentration range of zinc in air at remote sites (arctic) was $<0.003\text{--}0.027 \mu\text{g}/\text{m}^3$ (Barrie and Hoff 1985; Duce et al. 1975; Zoller et al. 1974). In aerosol samples of the lower troposphere collected over the Southern Bight of the North Sea between September 1988 and October 1989, the average zinc concentration was $67 \text{ ng}/\text{m}^3$ (standard deviation, $54 \text{ ng}/\text{m}^3$; range, $3\text{--}220 \text{ ng}/\text{m}^3$; $n = 108$ samples) (Injuk et al. 1992). The concentration of atmospheric zinc is usually lower in winter than in summer (Barrie and Hoff 1985; Daisey 1987).

Although data are sparse, higher-than-background concentrations have been reported near iron and steel-producing factories and zinc, lead, and copper smelters. During zinc smelting operations, concentrated zinc ore goes through a roasting procedure to convert zinc sulfide to zinc oxide. This process accounts for a large portion of the total atmospheric zinc emission during primary production (EPA 1980d). About 1.5 miles from a smelter in Kellogg, Idaho, Ragaini

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al. (1977) detected high annual mean concentrations of zinc in ambient air of $5 \mu\text{g}/\text{m}^3$. The 24-hour values for zinc ranged from 0.27 to $15.7 \mu\text{g}/\text{m}^3$; the average lead and cadmium concentrations at this smelter site were 11 and $0.8 \mu\text{g}/\text{m}^3$, respectively, indicating severe environmental pollution. Higher concentrations of zinc in the vicinity of a copper smelter than in reference areas were also reported by Patterson et al. (1977).

5.4.2 Water

In general, zinc is more concentrated in the sediments of streams and rivers than in the water column. It is reported by NAS (1977) that zinc will probably be detected in 75% of all water samples examined for zinc from various locations.

The zinc background concentrations in surface waters are usually less than $50 \mu\text{g}/\text{L}$ (EPA 1980d), but concentrations in different surface waters and groundwater can range from 0.002 to $50 \text{ mg}/\text{L}$ (NAS 1977). In many locations (e.g., New England, the southeast, the Missouri River basin, the Rio Grande River basin, and the Upper Colorado River basin), higher-than-background concentrations of zinc are common and appear to be correlated with mining activities in these areas and/or geological areas rich in zinc (EPA 1980d). However, in all river basins there are some locations with zinc concentrations of 0.1-1.0 mg/L (EPA 1980d).

The concentrations of zinc in water samples from Whitewood Creek, South Dakota, were measured by Hale (1977). The samples were collected upstream from the discharge of a local mining company. In 42 analyses, zinc concentrations ranged from <0.004 to $0.048 \text{ mg}/\text{L}$ with a mean concentration of $0.018 \text{ mg}/\text{L}$. The level of dissolved zinc in water from Lakes Erie and Ontario ranged from 3×10^{-6} to $1.1 \times 10^{-4} \text{ mg}/\text{L}$ (Coale and Flegal 1989).

Concentrations of zinc in surface water often correlate with the introduction of urban and industrial runoff. The Nationwide Urban Runoff Program (NURP), initiated to evaluate the significance of priority pollutants in urban storm water runoff, reports a frequency of detection for zinc of 95%, with a concentration range of 0.01-2.4 mg/L (Cole et al. 1984).

The concentrations of zinc in drinking water can be higher than concentrations in surface waters. Concentrations of 0.002-1.2 mg/L were detected in 77% of 1,577 surface water samples; levels of

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0.003-2.0 mg/L were found in 380 drinking water samples (NAS 1977). The higher concentrations in drinking waters are due to water treatment and to the distribution systems used for the water. Zinc in drinking water at levels as great as several mg/L was due to galvanized pipes and tanks in alkaline-water distribution systems. For example, drinking water samples from galvanized pipe plumbing systems in Seattle, Washington, contained zinc concentrations of 0.128-1.279 mg/L; these levels were >10 times higher than those in homes with copper pipe plumbing systems (Sharrett et al. 1982a). The results of analyzing 43 tap-water samples, collected in homes in Dallas, Texas, for trace metals reported maximum, minimum, median, and average concentrations of 0.049, 0.005, 0.011, and 0.0124 mg zinc/L, respectively (NAS 1977). The high zinc concentrations in these water samples were believed to be due to the household plumbing. In a study investigating associations between inorganic constituents of drinking water and cardiovascular diseases, Greathouse and Osborne (1980) collected and analyzed tap water samples in 35 geographic areas in the United States. From 100 to 110 tap-water samples were collected from each area. The maximum, minimum, and mean concentrations were 1.447, 0.025, and 0.144 mg zinc/L, respectively. Seventy-five percent of the zinc values were below 0.236 mg/L. Other investigators have also attributed the higher concentrations of zinc in household tap waters, compared to the raw originating water, to distribution and transmission lines (Maessen et al. 1985; Ohanian 1986; Schock and Neff 1988).

The available data suggest that zinc concentrations in drinking water are far less than the levels required to meet a daily intake level of 15 mg/day (assuming an adult water consumption of 2 L/day) (NAS 1977).

5.4.3 Sediment and Soil

Data on ambient concentrations of zinc in soil are limited. Zinc is generally found in soils at concentrations between 10 and 300 mg/kg, with a mean of ≈ 50 mg/kg (EPA 1980d). Zinc concentrations measured across the United States ranged from <5 to 400 mg/kg and from <10 to 2,000 mg/kg, with corresponding means of 36 and 51 mg/kg in cultivated and uncultivated subsurface soils, respectively (Connor and Shacklette 1975); however, these differences in zinc concentration may be attributed to differences in the soils prior to use (and not to cultivation). The sampling survey was designed to determine zinc concentrations of surficial materials unaltered from their natural condition. Soils near highways and smelters contained high zinc concentrations

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as a result of deposition of zinc released in tire abrasion and stack emissions (EPA 1980d). A study was designed by Hutchinson and Wai (1979) to investigate the distribution of cadmium, lead, and zinc in the soil and vegetation grown on it at two reclaimed waste dumps from phosphate ore mines in southeastern Idaho. Zinc concentrations in the soil of the waste dumps averaged from 443 ± 210 to $1,112 \pm 124$ mg/kg. These values were high compared with those found in the control plot (54216 mg/kg). Zinc concentrations in vegetation from the reclaimed waste dumps were also high compared to the control plot. Moderate-to-high levels of zinc contamination were found in leafy vegetables (lettuce) and their supporting soil in a zone with a 0-5-km radius around a copper smelter (Beavington 1975). The mean concentrations of zinc in 17 soil samples and 12 lettuce samples collected in this zone were 229 ± 17 and 316 ± 64 mg/kg dry weight, respectively. Significant relationships were found between the distance from the smelter and the levels of easily extractable zinc in the soil, and between the distance from the smelter and the content of zinc in herbage. Concentrations of zinc in soil irrigated with waste water or river water were measured by Schalscha et al. (1982). The total concentration of zinc in waste-water-treated soils was 228 mg/kg. The total concentration of zinc in soils irrigated with river water ranged from 103 to 136 mg/kg.

Municipal sludge and municipal incineration ash contain considerably higher levels of zinc than uncontaminated soils (Mumma et al. 1984, 1990, 1991). Therefore, application of sludge and municipal ash to soil will elevate the levels of zinc in these soils. The mean concentrations (mg/kg) of zinc according to four land use types were as follows: agricultural, 25; suburban residential, 75; mixed industrial/residential, 157; and industrial inner urban area, 360 (Haines 1984).

Since zinc in water is transported to the sediment in the adsorbed or precipitated state, the concentration of zinc in sediments of most waters is higher than the zinc concentration in aqueous phase. The concentration of zinc in Hamilton Harbor sediments ranged from 1,050 to 2,900 mg/kg, compared to zinc concentrations of 6-48 $\mu\text{g/L}$ in the aqueous phase (Mayer and Manning 1990). The concentrations of zinc in sediments of upper Columbia River, British Columbia, ranged from 45 to 51 mg/kg, while zinc concentrations in sediments from Lake Roosevelt, Washington, were 60-26,840 mg/kg (Johnson et al. 1990). The higher zinc concentrations in lake sediments were due to discharges from a lead-zinc smelter and a refinery. In the sediments of eight remote lakes in the Adirondack region of the northeastern United

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States, zinc concentrations in sediment cores ranged from 550 ± 140 mg/m² to 5620 ± 2680 mg/m² (Kada and Heit 1992).

5.4.4 Other Environmental Media

Bivalves and other sessile estuarine organisms are often used as a measure of contamination of estuarine water because they usually contain higher levels of metals than fish. The arithmetic mean concentration of zinc in oysters (*Crassostrea virginica*) from the Mississippi Sound collected in 1988 was 640 mg/kg (wet weight) (Lytle and Lytle 1990). In a nationwide mussel watch program, the mean concentrations of zinc in molluscs (*Mytilus edulis*) around the coast of the United States during 1976-1988 ranged from 67 to 3,700 mg/kg (dry weight) (Lauenstein et al. 1990). Although the concentration on a nationwide basis varied depending on sampling sites, the level of zinc showed little evidence of statistically significant change during 1976-1988. The mean concentration of zinc in oysters (*Crassostrea virginica*) collected from the U.S. coastline of the Gulf of Mexico during 1986-1988 was 2,150 mg/kg (dry weight) (Presley et al. 1990). In the National Contaminant Biomonitoring Program, the geometric mean concentration of zinc in various whole fish was 21.7 mg/kg (wet weight) (Schmitt and Brumbaugh 1990). Of all fish tested (e.g., bloater, sucker, white perch, bass, catfish, etc.), common carp showed the highest level of zinc. No significant trend in the level of zinc in whole fish was observed during 1978-1984. The concentration of zinc in yellow perch (*Perca flavescens*) from six acidic lakes in northwestern New Jersey ranged from 26.1 to 66.2 mg/kg (dry weight) (Sprenger et al. 1988). Although the concentrations of mercury and lead in fish from acidic lakes were higher compared to fish collected from non-acidic lakes, the concentrations of zinc showed no significant difference. Similarly, high concentrations of zinc were not found in white suckers (*Catostomus commersoni*) and brown bullheads (*Ictalurus nebulosus*) collected from two acidic Adirondack lakes in New York (Heit and Klusek 1985).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Zinc is ubiquitous in living organisms and ranks as one of the most abundant trace metals in humans. Humans are primarily exposed to zinc through ingestion. Sources of exposure include drinking water, food, air that is polluted, tobacco products, and occupational exposure. An average intake in humans is on the order of 0.14-0.21 mg zinc/kg/day (NAS 1977). The dietary

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intake of an average teenage male has been estimated to be so ≈ 0.27 mg zinc/kg/day, and dietary supplements may provide up to an additional 1 mg zinc/kg/day (EPA 1980d). In an extensive survey of foods in the total diets of individuals in the United States, conducted by the FDA during 1982-1984, the following values for daily zinc intakes (mg/day) were estimated in eight age and sex groups: 6-11-month-old infants, 5.24; 2-year-old children, 7.37; 14-16-year-old girls, 9.90; 14-16-year-old boys, 15.61; 25-30-year-old women, 9.56; 25-30-year-old men, 16.15; 60-65-year-old women, 8.51; and 60-85-year-old men, 12.64 (Pennington et al. 1986). Based on a body weight of 70 kg for a 25-30-year-old man, the intake corresponds to 0.23 mg/kg/day. The FDA included drinking water in the total diet. In a review of the literature, the National Research Council concluded that zinc concentrations in drinking water are generally well below 5 mg/L (NAS 1977). Assuming a daily intake of 2 L of water and an average body weight of 70 kg, a daily intake of less than 0.14 mg zinc/kg/day from drinking water can be estimated. Based on a body weight of 70 kg, the mean daily intakes of zinc in drinking water for residents of homes with galvanized and copper pipe plumbing systems in Seattle, Washington, were estimated to be 0.017-0.028 and 0.002-0.006 mg/kg/day, respectively (Sharrett et al. 1982b).

The NAS established the RDAs for zinc at 15 mg/day for men and 12 mg/day for women (NAS/NRC 1989b). The major source of zinc for the general population is food (EPA 1987~). Zinc is widespread in commonly consumed foods but tends to be higher in those of animal origin, particularly some seafoods (e.g., one serving of oysters will more than meet the daily dietary requirements of zinc) (NAS/NRC 1979). Meat products contain relatively high concentrations of zinc, whereas fruits and vegetables have relatively low concentrations. Generally, a person must eat a fairly high-protein diet to meet the RDA for zinc. Meats, fish, and poultry contained an average of 24.5 mg zinc/kg, whereas grains (or cereal products) and potatoes contained 8 and 6 mg/kg, respectively (Mahaffey et al. 1975). Zinc was present in all of the examined food classes. A diet of dairy products, meat, fish, poultry, grains, and cereals provides approximately 77% of the daily zinc intake. More recent data reported by the Food Safety and Inspection Service of the U.S. Department of Agriculture indicate that zinc was detected in 99.4-100% of the samples of healthy livestock and poultry randomly selected from among the specimens presented for slaughter in 1985-1986. Zinc concentrations in muscle tissue ranged from 0.20 ppm in young turkeys (n=61) to 1.92 ppm in heifers/steer (n=287) (Coleman et al. 1992). In a review of zinc levels in vegetables and other foods and beverages of plant origin, Weigert (1991) reported the following average concentrations (mg/kg): wheat - 41; rye - 13; rice - 8-20; potatoes - 3.51;

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vegetables - 4.31; fruit - 1.66; mushrooms - 9.7; cocoa - 35; tea - 35; and coffee - 6.7. Zinc has also been detected in wines from Seville, Spain, at concentrations of 0.3-5.40 pg/mL (Lopez-Artiguez et al. 1990). The FDA collected samples of foods representative of adult diets in 27 cities between October 1980 and March 1982 as part of its Total Diet Studies program (Gartrell et al. 1986a). Individual food items were separated into a number of food groups, and each was analyzed as a composite sample. The results for each food group were as follows:

<u>Food Group</u>	<u>Average Concentration (ppm)</u>	<u>Average Intake (mg/day)</u>
Dairy products	4.57	3.47
Meat, fish, and poultry	29.20	7.67
Grain and cereal products	8.68	3.64
Potatoes	4.82	0.77
Leafy vegetables	2.26	0.12
Legume vegetables	8.27	0.60

Federal regulations permit the use of zinc acetate, zinc oxide, and zinc sulfide as components of adhesives, coatings, or rubber packaging materials intended for food contact (FDA 1987b, 1987c, 1987d). Federal regulations also permit the use of zinc chloride, zinc oxide, zinc stearate, and zinc sulfate as GRAS (Generally Recognized As Safe) food additives when they are used “in accordance with good manufacturing practices” (FDA 1987e, 1987f, 1987g, 1987h, 1987i, 1987j). In addition, the use of zinc oxide as a color additive in drugs and cosmetics is also permitted with certain restrictions (FDA 1987a).

Negligible quantities of zinc are inhaled in ambient air. Exposure to airborne zinc is largely occupational through the inhalation of industrial dusts or fumes. Individuals occupationally exposed to metallic zinc and zinc compounds are those involved in galvanizing, smelting, welding, or brass foundry operations. In such operations, zinc as ore or metal and its alloys are often exposed in an oxidizing atmosphere to temperatures near the metal’s boiling point of 907°C. This heating results in the formation of fresh zinc oxide particles (0.2-1.0 µm), which may subsequently be inhaled. Inhalation of zinc oxide particles and fumes by workers can result in metal fume

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fever. Inhalation was reported to be the most probable route of exposure to zinc for 26 lead smelter workers found to have significantly ($p < 0.01$) elevated blood plasma levels of zinc. Mean plasma zinc concentrations were 12.9 mmol/L (range, 9.8-16.7) for the workers versus 10.9 mmol/L (range, 8.1-14.6) for a non-lead-exposed control group (Vasikaran et al. 1992).

Data from the National Occupational Exposure Survey (NOES), conducted by NIOSH from 1980 to 1983, indicate that 269 workers (including 22 women) in 22 plants were potentially exposed to pure zinc, and 133,608 workers (including 17,586 women) in 6,157 plants were potentially exposed to other forms of zinc (unknown composition) in the workplace in 1980 (NIOSH 1984b). All of the workers exposed to pure zinc were employed in the fabricated metal products industry as millwrights or assemblers. The largest numbers of workers exposed to other forms (unknown composition) of zinc worked in the primary metal industries, with fabricated metal products, with transportation equipment, with stone, clay, and glass products, and in special trade contractors industries. The occupational groups with the largest numbers of exposed workers were miscellaneous machine operators (not elsewhere classified or not specified), molding and casting machine operators, janitors and cleaners, and machinists. Exposure estimates were derived from observations of the actual use of the compound and the use of trade name products known to contain the compound.

The mean concentration of zinc in the fingernails and toenails of populations from the United States, Canada, and Japan were 105, 109, and 94 mg/kg, respectively (Takagi et al. 1988). The geometric mean concentrations of zinc in toenails (129 mg/kg) and scalp hair (108 mg/kg) of preschool children in Germany were about the same (Wilhelm et al. 1991). The total concentrations of zinc in 29 body tissues of 55 human cadavers were measured (Saltzman et al. 1990). The lowest concentration (mean of 1.5 ± 2.2 mg/kg [wet weight]) of zinc in both males and females was found in adipose tissues, while the highest concentrations were detected in the skull of males (mean of 54.3 mg/kg [wet weight]) and in the skeletal muscle of females (mean of 59.0 mg/kg [wet weight]). The mean concentrations of zinc in the feces of low-income urban Hispanics and rural Blacks in the United States were 75 and 94 mg/kg (wet weight), respectively (Prevost et al. 1985).

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5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Certain populations receive greater-than-average exposures to zinc from environmental sources. For example, higher levels of zinc have been reported in soil and water near waste sites, metal smelters, and areas exposed to untreated waste water (Hutchinson and Wai 1979; Ragaini et al. 1977; Schalscha et al. 1982). Other populations at risk of high exposure are those that have galvanized plumbing in their residences, and those that intentionally consume large doses of zinc as a dietary supplement. Patients who receive chronic treatment with drugs containing zinc salts (such as injectable insulin) are exposed to higher zinc levels than the general population. Allergic reactions to the zinc in insulin have been reported (Bruni et al. 1986). People in certain occupations are likely to be exposed to higher concentrations of zinc than the general population (see Section 5.5). However, the higher exposure may not be indicative of a long-term increase in body burden. For example, the median zinc concentration in the lung tissues of 21 Swedish workers previously employed in the refining and smelting of nonferrous metals was about the same as in a control group (11.0 versus 10.7 mg/kg [wet weight]) (Hewitt 1988). On the other hand, the median concentration of zinc in lung tissues of eight deceased coal miners from England was 72 mg/kg (wet weight) compared to a median value of 54 mg/kg (wet weight) for a control group (Hewitt 1988); however, the study author did not provide any evidence that the difference in zinc concentrations in the lungs of unexposed controls is statistically significant.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of zinc is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of zinc.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the

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identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. The available data adequately characterize the physical and chemical properties of the various forms of zinc to permit estimation of their environmental fate (ACGIH 1991; Baes and Sharp 1983; Baes et al. 1984; Gerritse et al. 1982; HSDB 1986, 1990; Merck 1983; NIOSH 1990; Weast 1988; Weiss 1986).

Production, Import/Export, Use, and Disposal. Zinc is a metallic element commonly found in ores in the earth's crust, and natural releases to the environment can be significant. Zinc is also one of the most widely used metals in the world (Mirenda 1986). In 1989, approximately 278,900 metric tons were produced from domestic ores in the United States (DOI 1991). The estimated world production from mines in 1989 was 7,062,000 metric tons. The production of zinc decreased from 1985 to 1987 but increased from 1987 to 1989 (DOI 1991). No estimates were located regarding current production. Zinc is most commonly used as a protective coating for other metals. It is also used in alloys such as bronze and brass, for electrical apparatus, and in organic chemical extractions. Zinc salts have numerous applications, including wood preservation. Zinc chloride is a primary ingredient in smoke bombs. In pharmaceuticals, zinc salts are used as solubilizing agents in drugs, including insulin (Lloyd 1984; Lloyd and Showak 1984; Merck 1983). Zinc oxide is found in ointments used to treat burns and infectious and skin diseases (EPA 1987d). Zinc is also utilized therapeutically in human medicine in the treatment of zinc deficiency (Elinder 1986). Zinc is also a food contaminant (EPA 1987~). The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgic operations involving zinc and use of commercial products containing zinc (EPA 1980d; NAS 1977; Nriagu and Pacyna 1988; Ragaini et al. 1977; TRI91 1993). Zinc has been detected in air, surface water, groundwater, and soil, with the frequency of detection and the concentrations greatest near source areas (e.g., hazardous waste sites and industrial areas such as lead smelters) (EPA 1980d; HAZDAT 1993; Lioy et al. 1978; Lloyd and Showak 1984; Mumma et al. 1984, 1990, 1991; NAS 1977). Current disposal methods are efficient (Dawson and Mercer 1986; Lloyd and Showak 1984). No data were located regarding the amount of zinc being disposed. There are rules and regulations regarding the disposal of zinc (Dawson and Mercer 1986; DOI 1991).

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According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 USC. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1991, became available in May of 1993. Environmental releases of zinc from manufacturing and processing facilities required to report their releases are listed in Table 5-1. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. Zinc partitions to the air, water, and soil (Callahan et al. 1979; Guy and Chakrabarti 1976; Houba et al. 1983; Pita and Hyne 1975). Zinc occurs in the environment mainly in the +2 oxidation state (Lindsey 1979). Adsorption is the dominant fate of zinc, resulting in enrichment of zinc in suspended and bed sediments (Callahan et al. 1979). The mobility of zinc in soil has been characterized (Baes and Sharp 1983; Bergkvist et al. 1989; EPA 1980d; Hermann and Neumann-Mahlkau 1985; Kalbasi et al. 1978; Saeed and Fox 1977; Tyler and McBride 1982). No estimate for the atmospheric lifetime of zinc is available. Development of pertinent data on the atmospheric processes important for zinc speciation in the atmosphere would be helpful. Development of this information would permit construction of a comprehensive model for the transport and interaction of zinc not only in air but in other media as well. Transformation in air and water can occur as a result of changes in chemical speciation (Anderson et al. 1988; Callahan et al. 1979; EPA 1980d; Stokinger 1981). Data that describe the transformation processes for zinc in soil or the fate of zinc in soil are needed. A model of zinc flux from all environmental compartments would be useful for providing information on the overall environmental fate of zinc.

Bioavailability. Zinc can be absorbed following inhalation (Drinker and Drinker 1928; Hamdi 1969), ingestion (Aamodt et al. 1983; Davies 1980; Johnson et al. 1988; Methfessel and Spencer 1973; NAWNRC 1979; Spencer et al. 1985) or dermal contact (Agren 1990; Gordon et al. 1981; Hallmans 1977; Keen and Hurley 1977). No estimates of the bioavailability of zinc after inhalation of zinc particles in air, ingestion from water and soil, or skin contact with bath water or soil were located. The bioavailability of zinc is higher in media with a low pH, as a result of increased zinc solubility and ionization. If zinc is partly present in an irreversibly adsorbed state in soil, this part is not available for skin absorption. It would be useful to develop quantitative data on the bioavailability of zinc from various environmental media.

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Food Chain Bioaccumulation. Zinc bioconcentrates moderately in aquatic organisms, and this bioconcentration is higher in crustaceans and bivalve species than in fish (EPA 1987~; Ramelow et al. 1989). Zinc does not concentrate in plants, and it does not biomagnify through the terrestrial food chain (Biddinger and Gloss 1984; Callahan et al. 1979; Hegstrom and West 1989; Levine et al. 1989).

Exposure Levels in Environmental Media. Zinc has been detected in air (Barrie and Hoff 1985; Duce et al. 1975; EPA 1980d; Evans et al. 1984; John et al. 1973; Liroy et al. 1978; Lloyd and Showak 1984; Patterson et al. 1977; Ragaini et al. 1977; Saltzman et al. 1985; Zoller et al. 1974) water (Coale and Flegal 1989; Cole et al. 1984; EPA 1980d; Hale 1977; HAZDAT 1993; Maessen et al. 1985; Minear et al. 1981; NAS 1977; Ohanian 1986; Schock and Neff 1988; Shiller and Boyle 1985; Windom et al. 1991), soil (Beavington 1975; Connor and Shacklette 1975; EPA 1980d; Haines 1984; HAZDAT 1993; Johnson et al. 1990; Mayer and Manning 1990; Mumma et al. 1984, 1990, 1991; Schalscha et al. 1982), and food (Coleman et al. 1992; Gartrell et al. 1986a; Mahaffey et al. 1975; Weigert 1991). However, since most of the data are not current, i.e., within the last 3 years, additional data would be useful to provide a more complete characterization of human exposure and the trend in zinc concentrations in various environmental media. Estimates have been made for human intake of zinc from food and drinking water (EPA 1980d; Gartrell et al. 1986a; NAS 1977; NAS/NRC 1989b; Pennington et al. 1986; Sharrett et al. 1982a, 1982b). Further data are needed on estimated daily intakes from inhalation resulting from occupational exposures.

Reliable monitoring data for the levels of zinc in contaminated media at hazardous waste sites are needed so that the information obtained on levels of zinc in the environment can be used in combination with the known body burden of zinc to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Exposure Levels in Humans. Zinc has been detected in fingernails, toenails, hair, all tissues, organs, skull and skeletal muscle, blood, feces, urine, sweat, and saliva (Greger and Sickles 1979; Hambidge et al. 1972; Henkin et al. 1975a; Llobet et al. 1988a; NASNRC 1979; Prasad et al. 1963a; Prevost et al. 1985; Saltzman et al. 1990; Schroeder et al. 1967; Takagi et al. 1988; Wastney et al. 1986; Wilhelm et al. 1991). Most of the data on occupational exposure levels of zinc are outdated (NIOSH 1976, 1984b). Additional information on potentially exposed workers

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and exposure levels would provide a more accurate characterization of occupational exposures in the United States. Current biological monitoring data on zinc are needed for populations surrounding hazardous waste sites.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Registries. No exposure registries for zinc were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

5.7.2 On-going Studies

No long-term research studies were located regarding the environmental fate of zinc. However, remedial investigations and feasibility studies on the NPL sites known to have zinc contamination are expected to be completed in the near future and may add to the current knowledge regarding the transport and transformation of zinc in the environment. In addition, environmental monitoring currently being conducted at NPL hazardous waste sites will likely add to the current database on environmental levels of zinc.

No long-term research projects or other on-going studies were located regarding occupational or general population exposures.